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(54) FLAME RETARDANT SELF-EXTINGUISHING POLYMER COMPOSITIONS

(71) We, AKZO NV, Arnhem/Nederland, IJsselaan 82, The Netherlands, a body corporate organised under the laws of The Netherlands; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to flame retardant, self-extinguishing polymer compositions. Numerous processes for the production of substantially non-inflammable textiles and other polymer compositions are known. A review of developments in this field is provided, for example, by the following works: Hans Vogel, "Flammfestmachen von Kunststoffen" (Flameproofing of Plastics), Dr. Alfred Huthig Verlag Heidelberg, 1966; John W. Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York . London . Toronto, 1970; Allec Williams, "Flame Resistant Fabrics", Noyes Data Corporation, Park Ridge, New Jersey, London, 1974. Reference is also made to the Supplement "Flammhemmende Textilien" (Flame-Resistant Textiles) from the Journal "Textilveredlung", Vol. 10, No. 5, May, 1975.

Known commercial flameproofing agents largely contain phosphorus, halogens and nitrogen.

In many cases, antimony, for example in the form of Sb₂O₃, is also added to the flameproofing agents to improve the flameproofing effect thereof, so that, in general, the flameproofed polymers contain relatively high percentages of additives. The incorporation of flameproofing agents of this quality and in this quantity into polymers is accompanied by a number of unfavourable secondary effects.

When added in effective quantities, flameproofing agents of the above type generally have an undesirable adverse effect upon the physical properties and service properties of the polymers. Thus, they generally produce a considerable deterioration in breaking strength, elongation, initial modulus, elasticity and adversely affect colour. In addition, despite the relatively large amount of flameproofing agents in the polymer, the flameproofing effect obtained is in many cases inadequate, especially in the case of filaments, so that only a few of the polymers flameproofed in this way are also self-extinguishing.

In many cases, conventional flameproofing agents are also largely incompatible with skin and are often physiologically harmful substances. Thus, numerous bromine-containing compounds cause irritation of the skin. Moreover, numerous phosphorus compounds, especially halogenated phosphoric acid esters, are highly toxic.

In addition, the conventional flameproofing agents which decompose during the burning process give off toxic and, in some cases, aggressive gases, such as hydrohalic acids, elemental halogen, halogen-oxygen compounds, oxides of nitrogen, nitrogen-halogen compounds and, in some cases, even hydrogen cyanide and dicyanogen. More-

over, in the case of synthetics, numerous conventional flameproofing agents cause accelerated degradation of the polymer melt during the burning process, thereby producing an increased dripping rate of, in some cases, burning polymer melt.

In cases where flameproofing agents are used in filaments and fibres, most conventional products produce only a temporary flameproofing effect because they may be washed out by repeated washing or dry cleaning.

Conventional flameproofing agents, especially those containing bromine, are relatively expensive. In addition, specialized techniques have to be developed for many of these flameproofing agents so that they may be incorporated into the polymer, for example specific dosage through mixers, metering pumps, the chemical aggressiveness of bromine compounds often giving rise to corrosion problems.

It has now surprisingly been found that, in contrast to the simple salts of oxalic acid, complex compounds of oxalic acid represent excellent flameproofing agents for polyamides, polyolefins, polyacrylates and epoxide resins. Hitherto, the use of oxalato complexes has only ever been mentioned in individual cases solely in conjunction with the flameproofing of polyamides by after-treatment with solutions of flameproofing agents.

In a process described in German Offenlegungsschrift No. 1,941,189 for the flameproofing of filler-containing polyamide moulding compositions or block graft polymers, mixtures of heavily brominated polyethers and antimony trioxide or antimony compounds are used as flameproofing agents. Antimony compounds are usually used as synergistic additives to halogen compounds, the effectiveness being ascribed to the antimony rather than to the remainder of the molecule. In addition to antimony (III) hydroxide, sodium antimonite, antimony chloride and antimony-potassium tartrate, complex antimony oxalates, such as $\text{Na}[\text{Sb}(\text{C}_2\text{O}_4)_2]$, are also mentioned as an example of an antimony compound. In this case, the oxalato complex represents only one of the possible antimony carriers. An independent flameproofing effect of the oxalic acid complexes is not mentioned in this Offenlegungsschrift.

A process for improving the flame resistance of natural and synthetic polyamide fibres using complex titanium compounds is known from German Offenlegungsschrift No. 2,152,196, the complex being formed with an organic chelate-forming agent or with fluorine ions. In this case, too, the oxalato complex is mentioned as only one of the possible heavy metal carriers, although citric acid and tartaric acid complexes are preferred. The flameproofing agent is generally applied to the textile material to be flameproofed from an aqueous solution. The process is said to be particularly suitable for wool and mixtures of wool and synthetic fibres, the flameproofing agent again being applied in the form of a treatment liquid. It is not surprising that this process is unsuitable for the flameproofing of completely synthetic fibres, especially the hydrophobic polyamides. In the case of mixtures of wool and synthetic fibres, it is, of course, only the wool component which is flameproofed. Accordingly, the use of oxalato complexes as flameproofing agents for polyamides, polyolefins, polyacrylates and epoxide resins is not suggested in this publication either.

The same also applies to the process described in German Auslegeschrift No. 2,212,718, according to which natural and synthetic polyamide fibres are said to be finished with anionic complexes of zirconium with an organic chelate-former or fluoride ions from aqueous solutions at pH values of from 0.5 to 4. In this case, too, the oxalato complex is mentioned in addition to purely inorganic compounds as one of the possible carriers for zirconium; in this case, too, the process is unsuitable for completely synthetic fibres.

The present invention relates to a process for the production of flame retardant and, optionally, self-extinguishing moulding compositions of polyamides, polyolefins, polyacrylates or epoxide resins, in which one or more oxalato complexes are introduced into the moulding composition as the sole flameproofing additive.

Oxalato complexes are coordination compounds comprising one or more central atoms, one or more ammonium or metal ions and one or more oxalato ligands.

In the context of the present invention, oxalato complexes are, in particular, complexes containing a complex anion of the type $[\text{Z}(\text{C}_2\text{O}_4)_n]^{-e}$, Z representing one or more central atoms, n being the number of ligands and $-e$ representing the negative charge of the complex anion. Oxalato complexes of this type are described in detail by K. V. Krishnamurti and G. M. Harris in Chemical Reviews, Vol. 61 (1961), pages 213 to 246. In general, there is one central atom, the number of ligands amounts to 1, 2, 3 or 4 and the charge of the complex anion to -1, -2, -3, -4 or -5, the number of ligands and the charge of the complex anion being determined by the co-ordination number and charge of the central atom. In the context of the present invention, oxalato complexes containing complex anions of the type $[\text{Z}(\text{C}_2\text{O}_4)_n]^{-e}$ comprise not only

compounds whose composition is exactly stoichiometric, but also compounds of the type in which the values for n and $-e$ differ from integers in the upward or downward direction. This is the case, for example, when a small number of the oxalato ligands is replaced by other ligands. Compounds of this type may be formed by incorporating or exchanging foreign ligands in the complex anion during or after synthesis of the oxalato complexes. The same also applies accordingly to the central atom, in other words the present invention also covers oxalato complexes of the type whose cationic constituent is not strictly stoichiometric in composition. Accordingly, the value for the central atom may also differ from an integer in this case, too. This will be the case when some of the central atoms are replaced by other central atoms having a different co-ordination number or a different valency. Such deviations from strict stoichiometry are encountered fairly frequently in complex chemistry and are well known to those skilled in the art.

The oxalato complexes used in accordance with the present invention also include mixed oxalato complexes which, instead of the stoichiometric quantity of a central atom, contain the corresponding quantity of different central atoms. It is, of course, also possible to use mixtures of different single or mixed oxalato complexes.

Central atoms of the oxalato complexes, especially in the preferred compounds containing a complex anion of the type $[Z(C_2O_4)_n]^{-e}$, are the metals Mg, Ca, Sr, Ba, Zr, Hf, Ce, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, B, Al, Ga, In, Sn, Pb and Sb. The cationic constituent of the oxalato complex preferably contains at least one of the ions Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ or NH_4^+ or one of the above-mentioned ions and Ba^{2+} .

Preferred oxalato complexes correspond to the following general formula:

$$Me_k^x Me_l^y [Z(C_2O_4)_m], \quad (1)$$

wherein Me^x represents Li, Na, K, Rb, Cs or NH_4 ; Me^y represents one of the above-mentioned cations or Ba; Z represents one of the central atoms Mg, Ba, Zr, Fe, Co, Cu, Zn, Al, Sn, Cr and Sb; $k \approx 0, 1, 2, 3$ or 4 ; $l \approx 0$ or 1 ; and $m \approx 2, 3$ or 4 .

(The symbol "≈" meaning "approximately equal to" is used here in order to make it clear once again that the values for k , l and m may differ from integers; cf. also Examples 1 to 14). Particularly preferred oxalato complexes are alkali-aluminium oxalato complexes corresponding to one of the following general formulae:

$Me_3^x [Al(C_2O_4)_6]$ or $Me^x [Al(C_2O_4)_2]$
and the oxalato complexes

$K_6 [Zn(C_2O_4)_3]$; $K_4 [Zr(C_2O_4)_4]$; $K_3 [Cr(C_2O_4)_3]$; $K_3 [Fe(C_2O_4)_3]$;
 $K_3 [Sb(C_2O_4)_3]$; $KBa [Fe(C_2O_4)_3]$; $KBa [Al(C_2O_4)_3]$; $K_2 [Mg(C_2O_4)_2]$;
 $K_2 [Fe(C_2O_4)_2]$; $K_2 [Zn(C_2O_4)_2]$; $K_2 [Cu(C_2O_4)_2]$ and $Ba [Mg(C_2O_4)_2]$.

The above-mentioned oxalato complexes represent a new class of compounds which are particularly suitable for use as flameproofing agents for polyamides, polyolefins, polyacrylates and epoxide resins. In general, the caesium complexes are the most effective, followed by the rubidium, potassium and sodium complexes and, finally, by the lithium complexes with, comparatively speaking, the lowest activity. Mixed alkali metal/barium complexes and the barium/magnesium complex also have a very good flame-proofing effect.

Compounds corresponding to general formula (1) above, wherein l represent O and Z represents Al, are complex lithium, sodium, potassium, rubidium, caesium, ammonium-aluminium dioxalato and aluminium-trioxalato salts with, co-ordinatively, a tetravalent or hexavalent aluminium atom. They are known and are readily obtained by precipitation from aqueous solutions of the components thereof, for example by reacting an aluminium sulphate solution with a lithium, sodium, potassium, rubidium, caesium or ammonium oxalate solution. So far as the processes used for the production of these complex salts, and the properties thereof, are concerned, reference is made to Gmelins Handbuch der Anorganischen Chemie, 8th Edition, "Aluminium", part B, Number 1, Verlag Chemie GmbH, Weinheim/Bergstr. 1933. Another process suitable for producing the potassium-aluminium trioxalate salt, in which freshly precipitated aluminium hydroxide is treated with an aqueous solution of potassium hydrogen oxalate, is described in Inorganic Synthesis, Vol. I, McGraw-Hill Book Comp., Inc., New York and London 1935, page 36. Of the oxalato complexes having other central atoms, most of the compounds used in accordance with the present invention are also known and adequately described. They may be obtained by reacting a salt of the central atom with alkali metal oxalate. Suitable compounds of the central atom

are, for example, sulphates, chlorides, hydroxides, acetates, carbonates and oxalates. Further information on the production of these complexes may be found in the following literature references:

5 D. P. Graddon, J. Inorg. and Nucl. Chem. 1956, Vol. 3, pages 308—322
 D. P. Graddon, Inorg. Syntheses, Vol. I, page 36
 K. V. Krishnamurty *et al.*, Chem. Rev. 61 (1961), pages 213—246.

10 Oxalato complexes, whose production is not explicitly described in the cited publications, may be similarly produced (see also the following Examples). In this case, too, the number of alkali metal and alkaline earth metal atoms, i.e. the value of k and l and the value of m , is, of course, determined by the valency of the central atom. Accordingly, the present invention also covers the use of compounds whose composition is not strictly stoichiometric in the sense of formula (1) above, i.e. *inter alia* compounds of the type in which the values for k , l and m differ slightly from integers in the upward or downward direction.

15 The flameproofing agents according to the present invention are particularly suitable for polyamides. Examples of polyamides are polyamides based on γ -butyrolactone (nylon 4), 6-aminocaproic acid or ϵ -caprolactam (nylon 6), 7-amino-oenanthic acid (nylon 7), 11-aminoundecanoic acid (nylon 11), 2-lauric lactam (nylon 12) and also polyamides based on dibasic carboxylic acids and diamines, such as polyhexamethylene adipic amide (nylon 66) and polyhexamethylene sebacic amide (nylon 610), and the aromatic polyamides, such as poly-*p*-benzamide or poly-*m*-benzamide. The oxalato complexes are also particularly suitable for use as flameproofing agents for polyacrylates, such as polyacrylonitrile, polymethacrylic esters and polyacrylic esters, and polyolefins, such as polyethylene, polypropylene, polybutylene, polyisobutylene and polystyrene, and also for epoxide resins. The compounds mentioned are intended to be understood in the broadest sense thereof, in other words they also include, for example, modified polymers, copolymers and copolycondensates.

20 The flameproofing agents used according to the present invention are suitable for all the conventional moulding compositions of the above-mentioned polymers. These compositions may be in the form of granulate, chips or strands, in the form of shaped articles, such as panels, sheeting, films and fibres, or in the form of finished textile products, such as yarns, knitted fabrics, non-wovens, cloths and carpets.

25 Little is known of the mechanism behind the oxalato complexes used as flameproofing agents in accordance with the present invention or of the principle behind the way in which they act. However, it is assumed that these compounds intervene not just at one stage of the combustion process, i.e. like halogenated flameproofing agents, for example, retard the combustion process by intervening in the radical chain, but instead the flameproofing effect according to the present invention is the result of several flame-inhibiting individual processes at various stages of the combustion process. The flameproofing agents used according to the present invention belong to the group of substances which give off inert gases. They have the advantage that they give off up to 4 moles of carbon dioxide per mole of starting substance. The most important principles behind the way in which they act are presumably the following: dissipation of thermal energy from the melt by dissociation of the flameproofing agent and heating of the inert gas, displacement and dilution of the oxygen at the surface of the burning polymer melt by the elimination of carbon dioxide, formation of oxide and salt layers during the combustion process and accelerated transport of radical acceptors, for example alkali metal atoms, into the gas phase.

30 It is clear that there is a connection between the decomposition temperature and the effectiveness of the flame-proofing agents used according to the present invention, on the one hand, and the polymers to be flameproofed, on the other hand, which must be taken into consideration in the choice of the oxalato complexes. Thus, an important condition for the effectiveness of the oxalato complexes is that the decomposition temperature thereof should be below the melting temperature of the burning polymer. On the other hand, the oxalato complexes must be completely chemically inert in the behaviour thereof up to the temperature at which moulding or shaping is carried out. Accordingly, oxalato complexes suitable for polyhexamethylene adipic amide should have a decomposition temperature which is above the processing temperature for polyhexamethylene adipic amide of about 280° C., but which does not exceed the temperature of the burning polyhexamethylene adipic amide melt of about 490° C. Where they are not already quoted in the literature, the decomposition temperature of the oxalato complexes may readily be determined by thermogravimetric analysis (TGA). So far as the carrying out of TGA is concerned, reference is made to Ullmanns

Encyklopädie der technischen Chemie, 3rd Edition (1961), Verlag Urban & Schwarzenberg, Munich-Berlin Vol. 2/1, page 657. Some examples of decomposition temperatures of various oxalato complexes are shown in the following Table:

Oxalato complex	Decomposition temperature °C
Rb ₃ [Al(C ₂ O ₄) ₃]	430
K ₃ [Al(C ₂ O ₄) ₃]	430
K ₃ [Fe(C ₂ O ₄) ₃]	440
K ₃ [Cr(C ₂ O ₄) ₃]	450
K ₄ [Zr(C ₂ O ₄) ₄]	395
K ₂ [Mg(C ₂ O ₄) ₂]	470
KBa [Al(C ₂ O ₄) ₃]	425

5 The melt temperature of the burning polymer, i.e. the temperature in the melt of the polymer burning in air, may be determined, for example, using a thermocouple. The measurement is best carried out in such a way that the soldered joint of the thermocouple is continuously covered by dripping melt during the measurement. 10 The following temperatures are examples of melt temperatures of burning polymers: Nylon 6,6: approx. 490° C; Perlon (Registered Trade Mark): approx. 400° C; polyethylene: approx. 410° C.

15 One extremely advantageous method of determining the decomposition temperature is differential thermoanalysis (DTA) because, in the DTA-diagrams of the oxalato complexes, the position of the endothermal main effect is indicative of the decomposition temperature. So far as differential thermoanalysis is concerned, reference is made to the relevant text books and hand books, for example to Ullmanns Encyklopädie der technischen Chemie, loc. cit. pages 656—657 and to Franke, Lexikon der Physik, Franckh'sche Verlags-Handlung Stuttgart, 3rd Edition.

20 Accordingly, when selecting suitable oxalato complexes as flameproofing agents for the above-mentioned polymers, it is best for the decomposition temperature of the oxalato complex and the melt temperature of the burning polymer to be brought as far as possible into line with one another. If one is confronted by the problem of having to flameproof a very specialized polymer, if the DTA values are not known and if, moreover, the instruments required for measuring the melt temperatures of the burning polymers and for the DTA-measurement are not available, it is possible to form, by means of a few empirical tests, a reliable picture as to which oxalato complexes may in fact be used and which of them provide optimum flameproofing. Naturally this also applies to the case where, despite the suitable position of the decomposition temperature of the oxalato complex and the melt temperature of the polymer, it is not possible to obtain satisfactory flameproofing for reasons which could not be foreseen.

25 The flame retardant polymers obtainable in accordance with the present invention may be processed into the conventional shaped articles, such as fibres, sheeting, films, panels and injection-moulded articles.

30 The complex salts used according to the present invention are excellent flameproofing agents. The two complex potassium salts K₃ [Al(C₂O₄)₃] and K₂ [Mg(C₂O₄)₂] and also the complex rubidium salt Rb₃ [Al(C₂O₄)₃], are particularly effective in polyamides. The last two of these compounds in particular are distinguished from the other complex salts by the fact that they largely prevent dripping of the melt during burning.

35 The oxalic acid complex salts used in accordance with the present invention develop a considerable flameproofing effect even in relatively small quantities. They are preferably used in quantities of from 1 to 40%, by weight, more especially from 5 to 15%, by weight, based on the flame retardant and, optionally, self-extinguishing polymer composition. The complex salts are preferably used in anhydrous form.

40 According to the present invention, a flame retardant and optionally self-extinguishing moulding composition is produced by introducing one or more of the

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oxalic acid complex salts according to the present invention into the polymer composition in the conventional way. This may be done *inter alia* by processes in which the flameproofing agent is actually added to the monomers during polyaddition, polymerisation or polycondensation and in this way is uniformly dispersed in the polymer formed. Another possible method of incorporation is to melt the polymer composition, to mix it with the flameproofing agent and then to process it into granulate or directly subject it to moulding or shaping. Another possible method is to scatter the finely divided flameproofing agent onto the polymer granulate and to process it with the polymer granulate. The particular procedure adopted will be determined by the particular field of application contemplated for the flame retardant and self-extinguishing moulding composition and may readily be selected by those skilled in the art.

In the case of relatively large or thick-walled mouldings, distribution of the flameproofing agent is relatively unproblematical and no difficulties are involved in producing the flameproofing agent in the suitable grain size for this purpose. By contrast, in the production of flame retardant and self-extinguishing fibres by the process according to the present invention, it is desirable to use the flameproofing agent in very finely divided form so that the polymer may be spun and to guarantee favourable physical properties for the end product. The suitable particle size is also governed by the particular field of application intended and may readily be selected by those skilled in the art. In the case of fibres, for example, it is determined by the denier of the fibres and by the required physical properties of the end product. In the case of textile fibres, the complex salts may be used in particle size of up to 2 μm .

No difficulties are involved in size-reducing the complex salts used in accordance with the present invention for example, they may readily be ground, in which case the adhering water and the water of crystallisation should be removed beforehand. In addition, drying of the complex salts does not involve any difficulties and is carried out, for example, over a period of several hours at 150° C./10mm Hg. The complex salts may be both dry-ground and also wet-ground. In the case of wet-grinding, the choice of the suitable dispersing liquid will also be determined by the particular sphere of application envisaged for the flameproofing agent and the manner in which it is applied.

In cases where polymers are reinforced with glass fibres, it should be noted that, in the case of glasses containing alkaline earths, especially calcium, the flame-proofing effect of the flameproofing agents according to the present invention is slightly impaired. It is assumed that this reduction in effectiveness is attributable to the presence of the alkaline earth, for example calcium, introduced into the polymer by way of the glass fibres. The calcium obviously reacts in the form of its oxide with the oxalato complex under melt conditions to form calcium oxalate and a complex reduced by one oxalato ligand. This reaction thus possibly leads to a successive degradation of the flame-proofing agent in the melt, so that the flameproofing agent may only be effective to a limited extent. It has been found that additives which are capable of binding alkaline earth, especially calcium, under the given conditions by the formation of stable calcium compounds, prevent the flameproofing effect from being impaired. Suitable additives are primarily such compounds as MgCO₃, MgSO₄, K₂C₂O₄, K₂CO₃, Al₂(SO₄)₃ and K₂SO₄. The additive is used in quantities of from 1 to 10%, by weight, preferably from 5 to 10%, by weight, based on the total weight of polymer, glass fibre, flameproofing agent and additive. However, even in the absence of the additional additives described above, the flameproofing effect obtained in cases where the above-mentioned glass fibres are used is still appreciable and sufficient for numerous applications.

The above-mentioned additives may, of course, also be used in the case of other reinforcing fillers containing alkaline earth and in cases where other additives containing alkaline earths are present.

The present invention relates to all the flame retardant and optionally self-extinguishing polymer compositions obtained by the processes described above using the above-mentioned oxalato complexes, especially those containing the oxalato complex in quantities of from 1 to 40%, by weight, preferably from 5 to 15%, by weight.

The complex salts used in accordance with the present invention have several advantages over conventional flameproofing agents. Firstly, it is pointed out that they may readily be obtained from the starting materials oxalic acid, an inorganic metal salt or metal hydroxide and, optionally, a simple inorganic alkali salt, the production thereof being carried out in aqueous solution. Apart from the complex rubidium and caesium salts, they are considerably less expensive than the conventional products containing halogen, phosphorus, nitrogen and/or Sb₂O₃.

Since the effectiveness of the complex salts and according to the present invention is greater than that of conventional flameproofing agents, they need only be added to the polymer in a quantity of a few percent, by weight, to obtain a comparable flameproofing effect. Accordingly, the characteristic properties of the treated materials are only modified to a fairly limited extent.

The compounds used according to the present invention are extremely compatible with the skin. Neither do they give off any toxic gases during the combustion process. Carbon dioxide is formed as the only gaseous combustion product of these substances. The polymer melt is largely prevented from dripping through the incorporation of the complex salts according to the present invention.

EXAMPLES 1 to 14.

To produce non-inflammable polyamide, nylon and Perlon chips were mixed in an extruder with 10 and 20%, by weight, of various oxalato complexes. The extrudate was processed into 2 mm thick polyamide films:

The associated Δ LOI-values are shown in Table 2.

The LOI-value was measured in accordance with ASTM—D 2863 by means of the measuring instrument manufactured by the Stanton Redcroft company of Great Britain.

The LOI-value (Limiting Oxygen Index) is defined as the oxygen content (in %) of an oxygen-nitrogen mixture at which a vertically mounted test specimen ignited at its upper end still just burns. The Δ LOI-value corresponds to the difference between the measured LOI-value of the flameproofed specimen and the LOI-value of the non-flameproofed specimen.

The following oxalato complexes were used:

$K_2[Mg(C_2O_4)_2]$

Produced by D. P. Graddon's method, J. Inorg. & Nucl. Chem. 1956, Vol. 3, page 321, Method 1:

38 g (0.206 mole) of potassium oxalate monohydrate were dissolved in 50 cc of water, the resulting solution heated to boiling point and a solution of 20.3 g (0.1 mole) of magnesium chloride in 100 cc of water added to it. The solution was then boiled for about another hour. After cooling to room temperature, the deposit was filtered off under suction, washed with water until free from chloride and finally dried *in vacuo* at 150° C. The yield amounted to 20 g (72% of the theoretical yield).

$K_2[Zn(C_2O_4)_2]/K_4 [Zn(C_2O_4)_3]$

Produced by D. P. Graddon's method described in J. Inorg. & Nucl. Chem. 1956, Vol. 3, page 321, method I:

A solution of 57.5 g (0.2 mole) of zinc sulphate heptahydrate in 200 cc of water was introduced with stirring into a hot solution of 36.8 g (0.2 mole) of potassium oxalate monohydrate in 100 cc of water. The zinc oxalate formed was filtered off under suction while still hot and washed with cold water. The zinc oxalate obtained in this way was then introduced into a boiling solution of 75 g (0.47 mole) of potassium oxalate monohydrate. The clear solution obtained was boiled for about 30 minutes, diluted with water to approximately 150 cc and cooled. A deposit was precipitated on rubbing with a glass rod. It was filtered off under suction and dried *in vacuo* first at 100° C. and finally at 150° C. The yield amounted to 54 g (55% of the theoretical yield). The substance consisted of a mixture of $K_4[Zn(C_2O_4)_3]$ and $K_2[Zn(C_2O_4)_2]$ and had a decomposition point of 395—430° C.

$K_4[Zr(C_2O_4)_4]$

23.3 g (0.1 mole) of zirconium chloride were dissolved in 150 cc of methanol. The solution was filtered and introduced, with stirring, at room temperature into a solution of 20 g (0.22 mole) of anhydrous oxalic acid in 100 cc of methanol. A deposit was precipitated. The reaction mixture was left standing at room temperature for about 20 hours and then filtered. The deposit was thoroughly washed with methanol, dissolved in 100 cc of water, filtered and, finally, introduced, while stirring, into a hot solution of 40 g (0.24 mole) of potassium oxalate monohydrate in 100 cc of water. The mixture was filtered while still hot and finally cooled. The deposit precipitated was filtered off under suction, washed with methanol and dried *in vacuo* at 150° C. The yield amounted to 43 g (72% of the theoretical yield).

TABLE 2

Example No.	Polymer	Complex Salt	Quantity of the complex %, by weight	ΔLOI
1	nylon	$K_2[Mg(C_2O_4)_2]$	10	2.5
2	PERLON	"	10	2.6
3	nylon	$K_2[Zn(C_2O_4)_2]$ / $K_4[Zn(C_2O_4)_3]$	10	1.0
4	PERLON	"	10	1.0
5	nylon	$K_4[Zr(C_2O_4)_4]$	20	2.6
6	PERLON	"	20	0.9
7	nylon	$KBa[Al(C_2O_4)_3]$	10	0.6
8	nylon	"	20	1.6
9	PERLON	"	10	0.9
10	PERLON	"	20	2.0
11	nylon	$K_3[Al(C_2O_4)_3]$	10	1.1
12	PERLON	"	10	1.6
13	nylon	$Rb_3[Al(C_2O_4)_3]$	10	2.6
14	PERLON	"	10	1.6
15	nylon	$K_2[Fe(C_2O_4)_2]$	10	3.9
16	PERLON	"	10	3.4
17	nylon	$KBa[Fe(C_2O_4)_3]$	10	4.4
18	PERLON	"	10	4.1

EXAMPLES 19 to 23.

To produce non-inflammable plastics, 10%, by weight, of $K_3[Al(C_2O_4)_3]$ were incorporated into various polymers in the conventional way. In most cases, both the polymer and also the flameproofing agent were finely ground and sifted, the powders subsequently mixed together, dried *in vacuo* for several hours at 150° C. and, finally, the mixture moulded under heat into test panels measuring 3×6.5×150 mm. In the case of the polycarbonates, the flameproofing agent was dispersed in a solution of the polymer in dichloromethane and the solvent subsequently removed with vigorous stirring at gradually increasing temperatures. The foam-like material obtained was dried *in vacuo* for 1 hour at 105° C., subsequently ground and, finally, moulded into test panels.

The LOI-value of these panels was determined in accordance with ASTM D 2863 and compared with the ΔLOI -values of a panel of the corresponding, but non-flame-proofed material. The polymer materials used and the ΔLOI -values obtained are shown in Table 3:

TABLE 3

Example No.	Polymer	ΔLOI -value
19	polypropylene (Vestolen P 6200, Huls)	1.6
20	polyacrylonitrile-butadiene-styrene (Terluran, BASF)	2.5
21	High-impact polystyrene (BASF)	1.0
22	epoxy resin Araldite (CIBA-GEIGY)	1.3
23	polymethylmethacrylate (Plexiglas)	1.9

("Vestolen", "Terluran", "BASF" and "Araldite" are Registered Trade Marks).

WHAT WE CLAIM IS:—

1. A process for the production of a flame retardant moulding composition of a polyamide, polyolefin, polyacrylate, or epoxide resin which comprises introducing one or more oxalato complexes into the moulding composition as the sole flame-proofing additive.

5 2. A process as claimed in claim 1 in which the oxalato complex contains a complex anion corresponding to the following general formula:



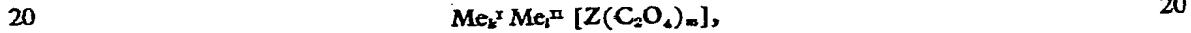
10 wherein Z represents one or more central atoms selected from Mg, Ca, Sr, Ba, Zr, Hf, Ce, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, B, Al, Ga, In, Sn, Pb and Sb.

n represents the number of ligands; and

—e represents the negative charge of the complex anion.

15 3. A process as claimed in claim 1 or claim 2 in which the cationic constituent of the oxalato complex contains at least one of the ions Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ or NH₄⁺ and may additionally contain Ba⁺⁺.

4. A process as claimed in any of claims 1 to 3 in which the oxalato complex corresponds to the following general formula:



in which

Me^x represents Li, Na, K, Rb, Cs or NH₄;

Me^l represents Li, Na, K, Rb, Cs, NH₄ or Ba;

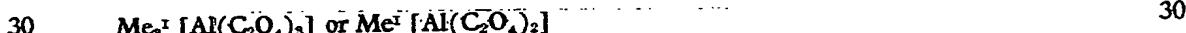
Z represents Mg, Ba, Zr, Fe, Co, Cu, Zn, Al, Sn, Cr or Sb;

k≈0, 1, 2, 3 or 4;

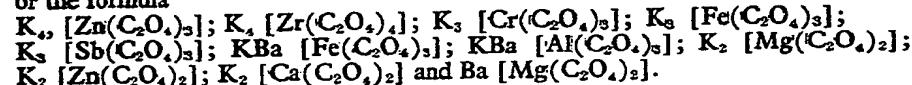
l≈0 or 1; and

m≈2, 3 or 4.

5. A process as claimed in any of claims 1 to 4 in which the oxalato complex corresponds to one of the general formulae:



or the formula



35 6. A process as claimed in any of claims 1 to 5 in which the moulding composition comprises a polyamide based on α -butyrolactone, 6-aminocaproic acid, ϵ -caprolactam, 7-aminoenanthic acid, 11-aminoundecanoic acid or 2-lauric lactam, polyhexamethylene adipic or sebacic amide; poly-*p*-benzamide or poly-*m*-benzamide.

7. A process as claimed in any of claims 1 to 6 in which the oxalato complex is used in a quantity of from 1 to 40%, by weight, based on the polymer composition.

40 8. A process as claimed in claim 7 in which the oxalato complex is used in quantity

of from 5 to 15%, by weight, based on the polymer composition.

9. A process as claimed in claim 1 substantially as herein described.

10. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

5 11. A flame retardant polyamide, polyolefin, polyacrylate or polyepoxide composition which contains one or more oxalato complexes as the sole flame-proofing additive.

12. A composition as claimed in claim 11 which is self-extinguishing.

13. A composition as claimed in claim 11 substantially as herein described.

14. A composition as claimed in claim 11 substantially as herein described with reference to any one of the Examples.

10 15. A composition as claimed in any of claims 11 to 14 when produced by a process as claimed in any of claims 1 to 10.

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